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(54) **Extended shelf life water-absorbing composition which facilitates fiber formation.**

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FR-A- 2 525 121
GB-A- 2 126 591
US-A- 3 085 986
US-A- 3 933 747
GB-A- 1 085 047
US-A- 2 418 688
US-A- 3 917 573

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Description

This invention relates to water-absorbing compositions.

In one of its more specific aspects, this invention relates to the incorporation of water-absorbing compositions into articles of manufacture for the purpose of improving the absorbent properties of the articles.

Absorbent compositions are widely used in the manufacture of products which require high absorption capability. For example, water-absorbing compositions are used in the manufacture of surgical and dental sponges, tampons, sanitary napkins and pads, bandages, disposable diapers, meat trays, and household pet litter. Water-absorbing compositions are also used for the modification of soil to improve water retention and increase air capacity and for a host of other applications.

As used herein, the term "water" when used in the phrases "water-absorbing" and "water-absorbent" is understood to mean not only water but also electrolyte solutions such as body fluids.

A number of absorbent compositions have been developed which exhibit water absorption capacity. For example, U.S. Pat. Nos. 3,954,721 and 3,983,095 disclose preparations for derivatives of copolymers of maleic anhydride with at least one suitable vinyl monomer in fibrous form. The fibrous copolymers are rendered hydrophilic and water-swellable by reaction with ammonia or an alkali metal hydroxide. U.S. Pat. No. 3,810,468 discloses lightly cross-linked olefin-maleic anhydride copolymers prepared as substantially linear copolymers and then reacted with a diol or a diamine to introduce cross-linking. The resultant lightly cross-linked copolymers are treated with ammonia or an aqueous or alcohol solution of an alkali metal hydroxide. U.S. Pat. No. 3,989,586 describes the preparation of sorptive paper products by incorporating cross-linked copolymers of styrene or olefins with maleic anhydride in a paper web which is then treated to convert the copolymer to a water-swellable salt form. U.S. Pat. No. 3,980,663 describes water-swellable absorbent articles made from carboxylic polyelectrolytes via cross-linking with glycerine diglycidyl ether. U.S. Pat. Nos. 4,332,917 and 4,338,417 disclose blends of copolymers of styrene and maleic anhydride with polymers derived from a monomeric ester having vinyl unsaturation e.g., poly(vinyl acetate), cellulose triacetate, cellulose aceto-butyrate, poly(ethylacrylate) and poly(methylmethacrylate). U.S. Pat. No. 4,420,588 teaches a water absorbing rubber composition comprising a 1,3-diene rubber and a water-absorbing resin dispersed in the rubber.

The desirability of having water-absorbing compositions in fibrous forms is well known. For example, in sanitary products such as disposable diapers and tampons, fibers can be more easily confined within the product. In this respect, the prior art water-absorbing compositions are deficient; they do not facilitate fiber formation. Because of the speed of their crosslinking reactions, the prior art water-absorbing compositions possess no appreciable shelf life; fiber formation must be completed shortly after the compositions are prepared. This shelf life deficiency in the prior art composition is discussed in U.S. Pat. No. 3,983,095 which teaches that fiber formation should be completed within several hours and in some cases immediately, depending upon the reactivity of the cross-linking agent used.

GB-A-2126591 describes the preparation of highly water absorbent polymers by crosslinking a polymer having carboxyl or carboxylate groups with a polyfunctional cross-linking agent such as polyethylene glycol in the presence of a controlled amount of water. Cross-linking is effected immediately after addition of the cross-linking agent and there is no suggestion that the product can be subjected to a subsequent shaping step. FR-A-2525121 is concerned with improving the absorbance of absorbable compositions which are in powder form. The improvement comprises treating the powdered form of an absorbable resin containing carboxy groups with a cross-linking agent such as a polyhydric alcohol to cross-link the molecular chains existing at least in the vicinity of the surface of the powder. The resin may be partially neutralised polyacrylic acid. The cross-linked product is a powder and there is no suggestion that it may be convertible to a shaped product such as a fibre or film.

The present invention provides water-absorbing compositions which possess excellent shelf life and have been found suitable for forming into fibers several months after preparation. They facilitate fiber formation over a wide range of time and temperature. They also possess excellent integrity in the hydrogel or water-swollen state, exhibit excellent water and electrolyte solution absorption capacity, and are readily incorporated into conventional water-absorbing products using conventional methods.

According to this invention there is provided an uncured aqueous composition which is stable at room temperature and heat curable and is water-absorbent upon curing said composition comprising:

a) a copolymer containing from 25 to 75 mole percent recurring units derived from at least one α,β-unsaturated monomer said units bearing at least one pendant carboxylic group selected from free carboxylic acid groups and neutralized carboxylic acid groups and from 20 to 80 percent of said pendant groups being neutralized carboxylic acid groups, and from 75 to 25 mole percent recurring units of at

least one comonomer copolymerizable with said α,β-unsaturated monomer; and

b) at least one monomer containing at least two hydroxyl groups.

Preferably, the monomer containing at least two hydroxyl groups is selected from alkylene glycols containing 2-10 carbon atoms and their ethers; cycloalkylene glycols; Bisphenol A; hydroxy alkylene derivatives of Bisphenol A; hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol; erythritol; pentaerythritol; and all natural monosaccharides.

The invention also provides a method of producing a water-absorbing composition which comprises heating the composition to cure it by reaction of the monomer (b) with the copolymer.

The invention further provides a method of absorbing water and electrolyte solutions comprising the step of contacting the water or electrolyte solution to be absorbed with the cured composition.

Also provided is an article of manufacture comprising the cured water-absorbing composition and means for supporting said composition to present said composition for absorption usage.

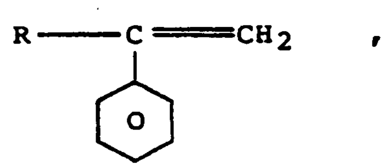
Yet further provided is a method of enhancing at least one water absorbing characteristic of an article which method comprises the step of incorporating into the article the cured water-absorbing composition, said composition being incorporated into the article in an effective amount to enhance at least one water-absorbing characteristic of the article as compared to the water-absorbing characteristics of the article in the absence of the composition.

Copolymers suitable for use to produce water-absorbing compositions of the invention will contain from 25 to 75 total mole percent of said recurring units bearing pendant carboxylic groups and from about 75 to about 65 total mole percent of recurring units bearing said pendant groups and from about 65 to about 35 total mole percent of at least one copolymerizable comonomer. Most preferably, the copolymer will be an equimolar copolymer.

Suitable α,β-unsaturated monomers are those bearing at least one pendant carboxylic acid unit or derivative of a carboxylic acid unit. Derivatives of carboxylic acid units include carboxylic acid salt groups, carboxylic acid amide groups, carboxylic acid imide groups, carboxylic acid anhydride groups and carboxylic acid ester groups.

Suitable α,β-unsaturated monomers include maleic acid; crotonic acid; fumaric acid; mesaconic acid; the sodium salt of maleic acid; the sodium salt of 2-methyl, 2-butene dicarboxylic acid; the sodium salt of itaconic acid; maleamic acid; maleamide; N-phenyl maleimide; maleimide; maleic anhydride; fuameric anhydride; itaconic anhydride; citraconic anhydride; mesaconic anhydride; methyl itaconic anhydride; ethyl maleic anhydride; diethylmaleate; methylmaleate and their mixtures.

Any suitable copolymerizable comonomer can be employed. Suitable copolymerizable comonomers include ethylene, propylene, isobutylene, C_1 to C_4 alkyl methacrylates, vinyl acetate, methyl vinyl ether, isobutyl vinyl ether, and styrenic compounds having the formula:



wherein R represents hydrogen or an alkyl group having from 1 to 6 carbon atoms and wherein the benzene ring may be substituted with low molecular weight alkyl or hydroxy groups.

Suitable C_1 to C_4 alkyl acrylates include methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate and their mixtures.

Suitable C_1 to C_4 alkyl methacrylates include methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propylmethacrylate, n-butyl methacrylate, and the like, and their mixtures.

And, suitable styrenic compounds include styrene, α-methylstyrene, p-methylstyrene, t-butyl styrene and their mixtures.

The pendant units on the α,β-unsaturated monomer will determine what, if any, additional reactions must be carried out to obtain a copolymer having the requisite pendant units necessary to produce the water-absorbing compositions of this invention, that is 20 to 80 percent pendant carboxylic acid units and 80 to 20 percent pendant carboxylate salt units. Preferably, both units are present in an amount of from 30 to 70 percent.

In general, if the α,β-unsaturated monomer bears only carboxylic acid amide, carboxylic acid imide, carboxylic acid anhydride, carboxylic acid ester groups, or mixtures thereof, it will be necessary to convert

at least a portion of such carboxylic acid derivative groups to carboxylic acid groups by, for example, a hydrolysis reaction. If the α,β-unsaturated monomer bears only carboxylic acid salt groups, acidification to form carboxylic acid groups will be necessary.

Similarly, the final copolymer must contain from 80 to 20 percent pendant carboxylate salt units. Accordingly, it may be necessary to carry out a neutralization reaction. Neutralization of carboxylic acid groups with a strong organic or inorganic base such as NaOH, KOH, ammonia, ammonia-in-water solution, or organic amines will result in the formation of carboxylate salt units, preferably carboxylate metal salt units.

Moreover, the sequence and the number of reactions (hydrolysis, acidification, neutralization, etc.) carried out to obtain the desired functionality attached to the copolymer backbone are not critical. Any number and sequence resulting in a final copolymer which possesses from 20 to 80 percent pendant carboxylic acid units and from 80 to 20 percent pendant carboxylate salt units is suitable.

One copolymer particularly suitable for use is a copolymer of maleic anhydride and isobutylene. Another is maleic anhydride and styrene. Suitable copolymers will have peak molecular weights of from about 5,000 to about 500,000 or more.

Suitable copolymers of maleic anhydride and isobutylene can be prepared using any suitable conventional method. Such copolymers are also commercially available from Kuraray Isoprene Chemical Company, Ltd., Tokyo, Japan, under the trademark ISOBAM. ISOBAM copolymers are available in several grades which are differentiated by viscosity molecular weight: ISOBAM-10, 160,000 to 170,000; ISOBAM-06, 80,000 to 90,000; ISOBAM-04, 55,000 to 65,000; and ISOBAM-600, 6,000 to 10,000.

To produce a water-absorbing composition of this invention, at least one copolymer as described above and at least one monomer bearing at least two hydroxyl groups are blended such that the water-absorbing composition contains preferably, in weight percent, from 80 to 99.5 total copolymer and from 0.5 to 20 of the said monomer. More preferably, the composition will contain from 90 to 99 weight percent total copolymer and from 1 to 10 weight percent total monomer.

Any suitable monomer bearing at least two hydroxyl groups and having a relatively low molecular weight, preferably less than 1,000, can be employed in the practice of this invention.

Suitable monomers include ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, 2-methyl 1,3-propane diol, neopentyl glycol, 1,5-pentane diol, diethylene glycol, dipropylene glycol, 1,4-cyclohexane dimethanol, Bisphenol A, 1,4-bis-(β-hydroxyethoxy)bis-phenol, hydroquinone, phloroglucinol, glycerol, erythritol, pentaerythritol, 1,7-dihydroxysedoheptulose.

Particularly suitable monomers for use in the practice of this invention are ethylene glycol, propylene glycol, 1,4-butane diol, diethylene glycol, and glycerol. A mixture of two or more of these may be used. Particularly preferred is a combination of 1,4-butane diol and pentaerythritol.

The water-absorbing composition of this invention can be prepared using any suitable blending method such as described in the examples which follow. After the water-absorbing composition is prepared, but typically before it is cured but some instances as it is curing, it is processed into any desired form using conventional methods of fabrication. For example, the water-absorbing composition can be subjected to casting; spray drying; air-assisted spray drying; air attenuation; wet, dry or flash spinning. The selection of the process is typically dictated by the shape or form needed for end use. Forms that the water-absorbing composition may be fabricated into include films or sheets, powders and granules, fibers and any form into which fibers can be processed such as for example milled fibers, chopped fibers, fluff or hulk fibers, strands, yarns, woven fabrics and non-woven mats using a variety of methods, including twisting, beaming, slashing, warping, quilling, severing, texturizing, weaving, knitting, braiding.

While not meaning to be limited to any theory, the monomer bearing at least two hydroxyl groups is believed to serve as a high temperature, slow-reacting, cross-linking type agent for the copolymer particles resulting in the formation of covalent cross-link type bonds upon curing. For example, it has been found that, if a partially neutralized styrene-maleic anhydride copolymer is blended with propylene glycol to form a water-absorbing composition according to this invention, a temperature about 150 °C. or higher is typically required to achieve cure. Similarly, if a partially neutralized ethylene-maleic anhydride copolymer is employed, a temperature of 140 °C. or higher is typically needed to achieve cure. And, if a partially neutralized isobutylene-maleic anhydride copolymer is employed, a temperature of 200 °C. or higher is typically needed to achieve cure.

Without meaning to limit the invention, the water-absorbing compositions of this invention are particularly well suited for being made into fibers because of the wide time and temperature ranges over which they can be shaped. More specifically, the water-absorbing compositions of this invention can be formulated to cure at temperatures within the range of from 140 °C to 250 °C. or higher and possess shelf lives in excess of two months as demonstrated in Example 7. Hence, the water-absorbing compositions of this

invention can be easily made into fibers using conventional fiber-forming methods and equipment. Moreover, no post-treatment (e.g., a salt-forming reaction as taught in U.S. Patent 3,983,095) of the cured fiber products is required.

The water-absorbing compositions of this invention and articles of manufacture into which the compositions are incorporated are suitable for use in a wide range of absorptive functions. In general, the articles into which the water-absorbing compositions are incorporated serve the function of supporting the composition and presenting it in a form adapted for absorptive end use. Means to support and present the composition for absorptive use include, but are not meant to be limited to bandages, surgical and dental sponges, tampons, sanitary napkins and pads, disposable diapers, meat trays, pads for absorption of perspiration.

In one embodiment, a water-absorbing composition of this invention is incorporated into a disposable diaper, using conventional fabrication methods to form a diaper composite having the following typical layers: (1) an outer layer (away from the body) of impermeable polyethylene film; (2) a first cellulosic pulp layer superimposed on the film; (3) a layer of (i) a cured water-absorbing composition of this invention in the form of, for example, fluff, a fibrous mass, a non-woven fiber mat or a woven fabric; or (ii) a layer comprising a blend of a cured water-absorbing composition of this invention and another fluff conventionally employed in diapers; (4) an optional, second cellulosic pulp layer; and (5) an inner permeable polyethylene film layer.

Fibers made from the water-absorbing compositions of this invention are particularly suitable for absorbent applications. It is well known that a mass of fibers provides a large surface area for contact with the liquid material to be absorbed. Fibers as compared to powders can also be more easily confined within the article into which they are incorporated.

The following examples serve to further demonstrate the invention.

EXAMPLE 1

This example demonstrates the preparation of a series of water-absorbing compositions of the invention using ISOBAM 10 isobutylene/maleic anhydride copolymer commercially available from Kuraray Isoprene Chemical Company, Limited. ISOBAM 10 has a molecular weight of 170,000 and a maleic anhydride content of about 59.3 weight percent (46.6 mole %) as determined by titration of maleic acid. Four water-absorbing compositions (I-IV) were separately prepared as follows.

About 1270 g of ISOBAM 10 isobutylene/maleic anhydride copolymer and about 2007 g of demineralized water were added to a mixing vessel with agitation and the vessel contents were heated to about 90 °C. At a temperature of about 90 °C about 658 g of a 50% sodium hydroxide solution prepared from 98.9% pure sodium hydroxide pellets were slowly added to the mixing vessel over a one hour period with agitation. After the addition of the sodium hydroxide solution, agitation was continued for about 12 hours at 90 °C. to complete the reaction.

The pH of the solution was found to be 6.5 and the neutralization reaction was calculated to have converted about 53.5% of the pendant carboxylic acid units on the 46.6 mole % anhydride units into carboxylate sodium salt units. The balance of the pendant units were converted to carboxylic acid units.

As shown in the following Table 1, four water-absorbing compositions of the invention were separately prepared using the above aqueous solution of partially neutralized isobutylene/maleic anhydride copolymer. Each of the four compositions was prepared by adding a predetermined amount of propylene glycol to a certain amount of copolymer solution and stirring for about 30 minutes. After stirring, each solution was separately heated to drive off excess water and to provide solutions of approximately a 45% solids content suitable for fiber formation using a dry spinning process.

TABLE 1

Composition	I	II	III	IV
Partially neutralized isobutylene/maleic anhydride copolymer solution (g)	213.25	203.57	198.83	222.52
Propylene glycol				
• (g)	2.06	3.29	4.49	7.18
• (phr) based on copolymer	3	5	7	10

Fibers having diameters of from about 5 - 25 x 10^{-3} mm (5-25 microns) were separately produced from Compositions I-IV by dry spinning. A sample of fibers produced from each composition was cured by heating at about 210°C. for 30 minutes and tested for absorbency. Each sample of fibers was tested to determine Swell Index and Percent Solubility using the following test procedures.

Swell Index

This test procedure is described in U.S. 4,454,055 the teachings of which are incorporated herein by reference thereto. The test procedure and equipment used herein were modified slightly as compared to the procedure and equipment described in U.S. 4,454,055.

To determine the Swell Index at atmospheric (room) pressure, about 0.2 to 0.3 g of the water-absorbing composition to be tested is placed in an empty W-shaped tea bag. The tea bag containing the composition is immersed in brine (0.9 wt.% NaCl) for 10 minutes, removed and allowed to sit on a paper towel for 30 seconds to remove surface brine. The Swell Index of the composition, that is, the units of liquid absorbed per each unit of sample is calculated using the following formula:

$$\text{Swell Index} = \frac{\text{Weight of Wet Composition}}{\text{Weight of Dry Composition}} - 1$$

To determine Swell Index under pressure, the following modified procedure was used.

After the tea bag containing the sample composition is immersed in brine and surface brine is removed, it is immediately placed in a 16 cm ID Buchner funnel fitted with a 2000 ml sidearm vacuum filter flask and connected to a manometer. Then, a piece of dental dam rubber sheeting is securely fixed over the mouth of the funnel such that the sheeting just rests on the tea bag. Next, a vacuum sufficient to create the desired pressure is drawn on the flask for a period of five minutes, and, the Swell Index under pressure is calculated using the above formula.

Percent Solubility

About 0.5 g of the water-absorbing composition sample to be tested is dispersed in about 150 g of brine (0.9 wt.% NaCl) at room temperature for 20 minutes with occasional gentle agitation. After 20 minutes, the mixture is filtered through a 0.15 mm (150 micron) polypropylene screen. Next, the filtrate is dried to a constant weight in an oven and the weight of soluble composition determined by subtracting the weight of the NaCl from the total weight of the dry filtrate. Percent solubility is then determined using the following formula:

$$\text{Percent Solubility} = \frac{\text{Weight of Soluble Composition}}{\text{Weight of Sample Composition}} \times 100$$

The test results for the fiber samples of Compositions I-IV are shown in Table 2.

TABLE 2

Composition	I	II	III	IV
Propylene glycol (phr)	3	5	7	10
Swell Index				
∘ Atmospheric Pressure	46.3	39.5	28.8	27.2
∘ 3.45 kPa(0.5 psi)	29.1	26.2	19.9	17.8
% Solubility	23.9	17.9	11.7	7.9

EXAMPLE 2

This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and ethylene glycol. Fibers produced from the composition were cured at different temperatures and the effect of curing at the different temperatures is shown in Table 3.

Using substantially the procedure of Example 1, about 226.13 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer produced in Example 1 were mixed with about 2.19 g of ethylene glycol and concentrated to give a 45% solids composition (Composition V) containing 3 phr of ethylene glycol based on the weight of the isobutylene/maleic anhydride copolymer. About 20 - 25 x 10^{-3} mm (20-25 micron) diameter fibers were prepared from the composition as described in Example 1. The absorbency of the fibers and the effect of three different cure temperatures, 190°C., 200°C., and 210°C. on samples of the fibers are shown in following Table 3.

TABLE 3

Composition	V	V	V
Cure Temperature (°C.)	190	200	210
Swell Index			
∘ Atmospheric Pressure	39.9	37.2	32.5
∘ 3.45 kPa(0.5 psi)	25.5	24.5	20.1
% Solubility	15.9	11.4	7.7

EXAMPLE 3

This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and 1,4-butane diol. Fibers produced from the composition were cured at different temperatures and the effect of curing at different temperatures is shown in Table 4.

Using substantially the procedure of Example 1, about 150.07 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer produced in Example 1 were mixed with about 3.39 g of 1,4-butane diol and concentrated to give a 45% solids composition (Composition VI) containing 7 phr of 1,4-butane diol based on the weight of the isobutylene/maleic anhydride copolymer. About 5 - 10 x 10^{-3} mm (5-10 micron) diameter fibers were prepared from the composition as described in Example 1. The absorbency of the fibers and the effect of three different cure temperatures, 170 °C., 180 °C., and 190 °C. on samples of the fibers are shown in following Table 4.

TABLE 4

Fibers of Composition	VI	VI	VI
Cure Temperature (°C.)	170	180	190
Swell Index			
∘ Atmospheric Pressure	39.4	36.4	27.5
∘ 3.45 kPa(0.5 psi)	25.9	23.5	16.2
% Solubility	15.1	8.0	5.4

EXAMPLE 4

This example demonstrates the preparation of different diameter fibers from a water-absorbing composition of this invention and shows the effect of fiber diameter on the absorbency of fibers of the same composition (Composition VII). Substantially the same materials and procedures of Example 1 were employed.

About 1270 g of isobutylene/maleic anhydride copolymer and about 2007 g of demineralized water were added to a mixing vessel with stirring and heated to about 90 °C. About 658.3 g of a 50% sodium hydroxide solution were added slowly over a one hour period. The reactor contents were stirred for about one hour, and then about 88.96 g (7 phr) of propylene glycol were added to the reactor. The reactor contents were stirred for about 9 hours at 90 °C.

A vacuum pump equipped with a cold trap was hooked to the top of the mixing vessel and excess water was removed to yield an aqueous solution having a solids content of about 55%.

The 55% solids solution was charged into a holding tank equipped with two 0.508 mm (0.020") nozzles located at the bottom of the tank. The solution was extruded through the nozzles under pressure into fibers which were wound onto a take-off roller. Fibers of different diameters were prepared by changing the speed of the take-off rollers and thus the speed at which fibers were drawn.

Four different diameter fibers were produced and cured at 210 °C. for about 30 minutes. The absorbency of the fibers and the effect of fiber diameter on the absorbency of the fibers are shown in Table 5.

TABLE 5

Fibers of Composition	VII	VII	VII	VII
Fiber Diameter 10^{-3}mm(microns)	10	25	100	175
Swell Index				
∘ Atmospheric Pressure	33.0	33.8	46.5	50.8
∘ 3.45 kPa(0.5 psi)	25.0	22.2	30.2	35.0
% Solubility	14.1	15.2	7.2	11.9

EXAMPLE 5

This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and glycerol. Fibers produced from the composition (Composition VIII) were cured at two different temperatures, and the effect of the different cure temperatures is shown in Table 6.

Using substantially the procedure of Example 1, about 2869 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer of Example 1 were mixed with 64.8 g of glycerol and concentrated to give a 45% solids composition containing 7 phr glycerol based on the weight of the isobutylene/maleic anhydride copolymer. Samples of fibers having diameters of about 10 microns were produced by dry spinning and separately cured at 170°C. and 180°C. for 30 minutes and tested for absorbency. The test results are shown in Table 6.

TABLE 6

Fibers of Composition	VIII	VIII
Cure Temperature (°C.)	170	180
Swell Index		
∘ Atmospheric Pressure	43.8	34.2
∘ 3.45 kPa(0.5 psi)	28.3	24.9
% Solubility	16.7	11.7

EXAMPLE 6

This example demonstrates the preparation of a water-absorbing composition of this invention using ISOBAM 10 isobutylene/maleic anhydride copolymer and diethylene glycol. Fibers produced from the composition (Composition IX) were cured at two different temperatures, and the effect of the different cure temperatures is shown in Table 7.

Using substantially the procedure of Example 1, about 109.22 g of the aqueous solution of the partially neutralized isobutylene/maleic anhydride copolymer of Example 1 were mixed with 2.47 g of diethylene glycol and concentrated to give a 45% solids composition containing 7 phr diethylene glycol based on the

weight of the isobutylene/maleic anhydride copolymer. Samples of fibers having diameters of about 10 - 20 x 10^{-3} mm (10-20 microns) were produced by dry spinning and separately cured at 170°C. and 180°C. for 30 minutes and tested for absorbency. The test results are shown in Table 7.

TABLE 7

Fibers of Composition	IX	IX
Cure Temperature (°C.)	170	180
Swell Index		
∘ Atmospheric Pressure	58.8	38.3
∘ 3.45 kPa(0.5 psi)	41.3	32.9
% Solubility	21.6	12.7

EXAMPLE 7

This example demonstrates that the water-absorbing compositions of this invention possess excellent shelf-life in solution form.

A sample of the aqueous solution prepared according to the procedure of Example 5 was aged at 90°C in a closed container. Solution viscosity measurements using a Brookfield viscometer were taken after 6, 29, 35 and 41 hours aging. The viscosities measured are listed in Table 8, below. After 41 hours no gel formation was observed in the solution.

TABLE 8

Composition (aqueous solution)	VIII
Aging Time at 90°C	Viscosity (Poises)
0 hr	700
6 hrs	773
29 hrs	802
35 hrs	757
41 hrs	776

Another sample of the aqueous solution of Example 5 was aged for 11 weeks at ambient temperature. After 11 weeks aging, fibers were prepared from the aged solution and the resulting fibers were cured at 180°C for 30 minutes.

The absorbent property data of the resulting fibers prepared after 11 weeks compared with the absorbent property data of the fibers produced from the same composition (Example 5) but in the absence of aging, the composition is shown in Table 9.

TABLE 9

Fiber of Composition	VIII	VIII
Time of Solution Aging	0	11 weeks
Swell Index:		
∘ Atomospheric Pressure	34.2	41.2
∘ 3.45 kPa(0.5 psi)	24.9	30.3

The above data demonstrate that fibers of the invention produced after eleven weeks aging from the composition of Example 5 do not lose their absorbent properties as compared to the absorbent properties of fibers prepared in the absence of aging.

Claims

1. An uncured aqueous composition which is stable at room temperature and heat curable and is water-absorbent upon curing said composition comprising:
   a) a copolymer containing from 25 to 75 mole percent recurring units derived from at least one α,β-unsaturated monomer said units bearing at least one pendant carboxylic group selected from free carboxylic acid groups and neutralized carboxylic acid groups and from 20 to 80 percent of said pendant groups being neutralized carboxylic acid groups, and from 75 to 25 mole percent recurring units of at least one comonomer copolymerizable with said α,β-unsaturated monomer; and
   b) at least one monomer containing at least two hydroxyl groups.

2. A composition as claimed in claim 1 which said copolymer contains from 35 to 65 mole percent recurring units of said at least one α,β-unsaturated monomer and from 65 to 35 mole percent of said at least one copolymerizable comonomer.

3. A composition as claimed in claim 2 in which the copolymer is an equimolar copolymer.

4. A composition as claimed in any one of claims 1 to 3 in which said copolymer is derived from copolymers of styrene and maleic anhydride, copolymers of ethylene and maleic anhydride, and copolymers of isobutylene and maleic anhydride.

5. A composition as claimed in any one of claims 1 to 4 wherein said monomer (b) is selected from alkylene glycols containing 2-10 carbon atoms; cycloalkylene glycols; Bisphenol A, hydroxy alkylene derivatives of Bisphenol A, hydroquinone; phloroglucinol; hydroxy alkylene derivatives of diphenols; glycerol, erythritol, pentaerythritol, and natural monosaccharides.

6. A composition as claimed in any one of claims 1 to 5 wherein said monomer (b) has a molecular weight below 1000.

7. A composition as claimed in claim 6 in which said monomer (b) is selected from ethylene glycol, propylene glycol, 1,4-butane diol, diethylene glycol, glycerol and pentaerythritol, and mixtures of two or more thereof.

8. A composition as claimed in claim 7 in which said monomer (b) is a mixture of 1,4-butane diol and pentaerythritol.

9. A composition as claimed in any one of claims 1 to 8 comprising in weight percent from 80 to 99.5 of said copolymer and from 0.5 to 20 of said monomer (b).

10. A composition as claimed in claim 9 comprising in weight percent from 90 to 99 of said copolymer and from 1 to 10 of said monomer (b).

11. A composition as claimed in any one of claims 1 to 10 wherein from 30 to 70 percent of the pendant groups are neutralized carboxylic acid groups.

12. A method of producing a water-absorbing composition comprising heating an aqueous composition as claimed is any one of claims 1 to 11, to cure it by reaction of monomer (b) with the copolymer.

13. A method as claimed in claim 12 in which the aqueous composition is formed into a shaped article before it is fully cured.

14. A method as claimed in claim 13 in which the shaped article is selected from fiber, powder and film.

15. A method as claimed in any one of claims 12 to 14 in which the composition is heated to a temperature of at least 140 °C.

16. An article of manufacture comprising a cured water-absorbing composition as claimed in any one of claims 1 to 11, or formed by the method claimed in any one of claims 12 to 15, and a means for supporting said composition for absorption usage.

17. An article as claimed in claim 16 in which said means for supporting said composition is selected from disposable diapers, tampons, sanitary napkins, surgical and dental sponges and bandages.

18. A method of absorbing water and electrolyte solutions comprising the step of contacting the water or electrolyte solution to be absorbed with a composition as claimed in any one of claims 1 to 11 which has been cured or a cured composition obtained by the method of any one of claims 12 to 15.

Patentansprüche

1. Ungehärtete wäßrige Zusammensetzung, die bei Raumtemperatur stabil und durch Hitze härtbar ist und bei Härtung wasserabsorbierend wird, umfassend
   a) ein Copolymer enthaltend 25 bis 75 Mol% wiederkehrende Einheiten, die aus mindestens einem α-β-ungesättigten Monomer abgeleitet sind und mindestens eine carboxylische Seitengruppe tragen, die aus freien Carbonsäuregruppen und neutralisierten Carbonsäuregruppen besteht, wobei 20 bis 80 % dieser Seitengruppen neutralisierte Carbonsäuregruppen sind, und 75 bis 25 Mol% wiederkehrende Einheiten von mindestens einem mit diesem α-β-ungesättigten Monomer copolymerisierbaren Comonomer, und
   b) mindestens ein Monomer, das mindestens zwei Hydroxylgruppen enthält.

2. Zusammensetzung nach Anspruch 1, in der das Copolymer 35 bis 65 Mol% wiederkehrende Einheiten des mindestens einen α-β-ungesättigten Monomeren und 65 bis 35 Mol% des mindestens einen copolymerisierbaren Comonomeren enthält.

3. Zusammensetzung nach Anspruch 2, in der das Copolymer ein äquimolares Copolymer ist.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, in der das Copolymer von Copolymeren aus Styrol und Maleinsäureanhydrid, Copolymeren aus Ethylen und Maleinsäureanhydrid und Copolymeren aus Isobutylen und Maleinsäureanhydrid abstammt.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, in der das Monomer (b) aus Alkylenglykolen mit 2 bis 10 Kohlenstoffatomen, Cycloalkylenglykolen, Bisphenol A, Hydroxyalkylenderivaten von Bisphenol A, Hydrochinon, Phlorglucin, Hydroxyalkylenderivaten von Diphenolen, Glycerin, Erythrit, Pentaerythrit und natürlichen Monosacchariden ausgewählt ist.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, in der das Monomer (b) ein Molekulargewicht unter 1000 hat.

7. Zusammensetzung nach Anspruch 6, in der das Monomer (b) aus Ethylenglykol, Propylenglykol, 1,4-Butandiol, Diethylenglykol, Glycerin und Pentaerythrit sowie Mischungen aus zwei oder mehreren dieser Substanzen ausgewählt ist.

8. Zusammensetzung nach Anspruch 7, in der das Monomer (b) eine Mischung aus 1,4-Butandiol und Pentaerythrit ist.

9. Zusammensetzung nach einem der Ansprüche 1 bis 8, die 80 bis 99,5 Gew.% des Copolymers und 0,5 bis 20 Gew.% des Monomeren (b) umfaßt.

10. Zusammensetzung nach Anspruch 9, die 90 bis 99 Gew.% des Copolymers und 1 bis 10 Gew.% des Monomeren (b) umfaßt.

11. Zusammensetzung nach einem der Ansprüche 1 bis 10, in der 30 bis 70 % der Seitengruppen neutralisierte Carbonsäuregruppen sind.

12. Verfahren zur Herstellung einer wasserabsorbierenden Zusammensetzung, bei dem man eine wäßrige Zusammensetzung nach einem der Ansprüche 1 bis 11 erhitzt, um sie durch Reaktion des Monomeren (b) mit dem Copolymer zu härten.

13. Verfahren nach Anspruch 12, bei dem die wäßrige Zusammensetzung vor ihrer vollständigen Aushärtung zu einem Formgegenstand verformt wird.

14. Verfahren nach Anspruch 13, bei dem der Formgegenstand aus Faser, Pulver und Film ausgewählt ist.

15. Verfahren nach einem der Ansprüche 12 bis 14, bei dem die Zusammensetzung auf eine Temperatur von mindestens 140 °C erhitzt wird.

16. Produkt, das eine gehärtete wasserabsorbierende Zusammensetzung nach einem der Ansprüche 1 bis 11 enthält oder nach einem der Ansprüche 12 bis 15 verformt ist sowie einen Träger für die Zusammensetzung zu Absorptionszwecken umfaßt.

17. Gegenstand nach Anspruch 16, bei dem der Träger für die Zusammensetzung aus Wegwerfwindeln, Tampons, Monatsbinden, chirurgischen Schwämmen, Dentalschwämmen und Verbänden ausgewählt ist.

18. Verfahren zur Absorption von Wasser und Elektrolytlösungen, bei dem man das zu absorbierende Wasser bzw. die Elektrolytlösung mit einer gehärteten Zusammensetzung nach Anspruch 1 bis 11 bzw. einer Zusammensetzung, die durch das Verfahren nach einem der Ansprüche 12 bis 15 erhalten wurde, in Kontakt bringt.

Revendications

1. Composition aqueuse non durcie, qui est stable à la température ambiante, durcissable sous l'action de la chaleur et qui absorbe l'eau après durcissement, ladite composition, comprenant :
   a) un copolymère contenant de 25 à 75 % en moles d'unités récurrentes provenant d'au moins un monomère α,β-insaturé, lesdites unités portant au moins un groupe carboxylique pendant choisi parmi des groupes d'acides carboxyliques libres et des groupes d'acides carboxyliques neutralisés, 20 à 80 % desdits groupes pendants étant des groupes d'acides carboxyliques neutralisés, et de 75 à 25 % en moles d'unités récurrentes d'au moins un comonomère copolymérisable avec ledit monomère α,β-insaturé ; et
   b) au moins un monomère contenant au moins deux groupes hydroxyles.

2. Composition selon la revendication 1, dans laquelle ledit copolymère contient de 35 à 65 % en moles d'unités récurrentes dudit monomère α,β-insaturé minimal et de 65 à 35 % en moles dudit comonomè-

re copolymérisable minimal.

3. Composition selon la revendication 2, dans laquelle le copolymère est un copolymère équimolaire.

4. Composition selon l'une quelconque des revendications 1 à 3, dans laquelle ledit copolymère provient de copolymères de styrène et d'anhydride maléique, de copolymères d'éthylène et d'anhydride maléique, et de copolymères d'isobutylène et d'anhydride maléique.

5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle ledit monomère (b) est choisi parmi des alkylèneglycols contenant de 2 à 10 atomes de carbone, des cycloalkylèneglycols, le bisphénol A, des dérivés hydroxyalkylène de bisphénol A, l'hydroquinone, le phloroglucinol, des dérivés hydroxyalkylène de diphénols, le glycérol, l'érythritol, le pentaérythritol et des monosaccharides naturels.

6. Composition selon l'une quelconque des revendications 1 à 5, dans laquelle ledit monomère (b) a un poids moléculaire de moins de 1 000.

7. Composition selon la revendication 6, dans laquelle ledit monomère (b) est choisi parmi l'éthylèneglycol, le propylèneglycol, le 1,4-butanediol, le diéthylèneglycol, le glycérol et le pentaérythritol, et des mélanges de deux de ces composés ou plus.

8. Composition selon la revendication 7, dans laquelle ledit monomère (b) est un mélange de 1,4-butanediol et de pentaérythritol.

9. Composition selon l'une quelconque des revendications 1 à 8, comprenant de 80 à 99,5 % en poids dudit copolymère et de 0,5 à 20 % en poids dudit monomère (b).

10. Composition selon la revendication 9, comprenant de 90 à 99 % en poids dudit copolymère et de 1 à 10 % en poids dudit monomère (b).

11. Composition selon l'une quelconque des revendications 1 à 10, dans laquelle de 30 à 70 % des groupes pendants sont des groupes d'acides carboxyliques neutralisés.

12. Procédé de préparation d'une composition absorbant l'eau, comprenant le chauffage d'une composition aqueuse selon l'une quelconque des revendications 1 à 11 pour la faire durcir grâce à la réaction du monomère (b) avec le copolymère.

13. Procédé selon la revendication 12, dans lequel on transforme la composition aqueuse en un article façonné avant qu'elle soit complètement durcie.

14. Procédé selon la revendication 13, dans lequel l'article façonné est choisi parmi des fibres, des poudres et des films.

15. Procédé selon l'une quelconque des revendications 12 à 14, dans lequel la composition est chauffée à une température d'au moins 140 °C.

16. Article fabriqué comprenant une composition durcie absorbant l'eau selon l'une quelconque des revendications 1 à 11, ou formé au moyen du procédé selon l'une quelconque des revendications 12 à 15, et un moyen pour supporter ladite composition, utilisé comme absorbant.

17. Article selon la revendication 16, dans lequel le moyen servant à supporter ladite composition est choisi dans l'ensemble constitué par des couches jetables, des tampons, des serviettes hygiéniques, des éponges chirurgicales et dentaires et des bandages.

18. Procédé d'absorption d'eau et de solutions d'électrolytes, comprenant l'étape consistant à amener l'eau ou la solution d'électrolyte à absorber au contact d'une composition selon l'une quelconque des revendications 1 à 11, qui a été durcie, ou d'une composition durcie qu'on a obtenue au moyen du procédé selon l'une quelconque des revendications 12 à 15.